Energy Transfer Mechanism in $Gd_2(SiO_4)O$:Ce Scintillators

H. Suzuki* and T. A. Tombrello
Division of Physics, Mathematics, and Astronomy,
California Institute of Technology, Pasadena, CA 91125

C. L. Melcher and J. S. Schweitzer
Schlumberger-Doll Research, Old Quarry Road, Ridgefield, CT 06877-4108

Abstract

The scintillation decay of cerium-doped gadolinium oxyorthosilicate $Gd_2(SiO_4)O$:Ce is lengthened by the energy transfer from Gd to Ce. To investigate the role of the Gd in the scintillation processes, the Gd was partially replaced by optically inactive rare earth elements, Y and Lu, and the effective transfer rates from Gd to Ce were measured as a function of Gd and Ce concentrations using UV- and gamma-ray excitations. The data clearly indicate the dilution of the Gd by the Y and the Lu further lengthens the migration time through the Gd in the energy transfer process from Gd to Ce.

I. INTRODUCTION

Gadolinium oxyorthosilicate $Gd_2(SiO_4)O$ [1] has a high density (6.7 g/cm^3) and a high effective atomic number (59) for the efficient detection of x- and γ-radiation. Therefore, if $Gd_2(SiO_4)O$, which has an energy gap of ~6 eV, is used as a scintillator, it is expected to be optically transparent and be an ideal environment to an efficient and fast light emitting activator, the Ce^{3+} ion. However, the 4f-4f transitions of Gd^{3+} ions are of an energy where energy localized in Gd^{3+} can be transferred to the Ce^{3+} activator [2]. This energy transfer from Gd (donor or "D") to Ce (acceptor or "A") lengthens the light emission time of the Ce^{3+}, which limits timing applications of $Gd_2(SiO_4)O$:Ce (GSO) [3] . The light emission mechanism of the Ce^{3+} in GSO is well understood [4]; the overall scintillation processes of GSO are still unclear. Previously, the dependence of scintillation properties on Ce concentration was investigated [5]. To examine the role of the Gd in the scintillation processes, we diluted Gd with optically inactive rare earth elements, Y and Lu, and analyzed the decay kinetics of Ce^{3+} emission using UV- and gamma-ray excitations. The Gd^{3+} emission could not be measured because of its weak intensity; this limits our understanding of the Gd^{3+} decay, the nature of donor-donor and donor-acceptor interactions, and the migration mechanism among Gd^{3+} ions. The dilution of Gd is expected to increase the average Gd-Gd distance and to slow the migration of energy between Gd ions, and slow the transfer from Gd to Ce. Our results confirm that the transfer from Gd to Ce becomes slower, i.e., the decay of the Gd^{3+} becomes longer, as the Y (or Lu) concentration increases.

* Present address: Schlumberger-Doll Research, Old Quarry Road, Ridgefield, CT 06877-4108.

When GSO absorbs the energy of the incident radiation, many electrons, holes and excitons are created. Some electrons, holes and excitons migrate through the GSO crystal to excite the Ce^{3+} and recombine. We can thus separate the scintillation mechanism into two parts: primary and secondary processes [6]. The primary processes are the transfer of energy from the ionizing radiation to the luminescent centers (Ce^{3+}); the secondary processes are the processes by which excited Ce^{3+} ions lose their energy. We studied the secondary processes by directly exciting the Ce^{3+} using UV excitation [4]. We proposed that GSO has two different activation centers (Ce1 and Ce2), because the host rare earth, Gd, occupies two different crystallographic sites in GSO [7].

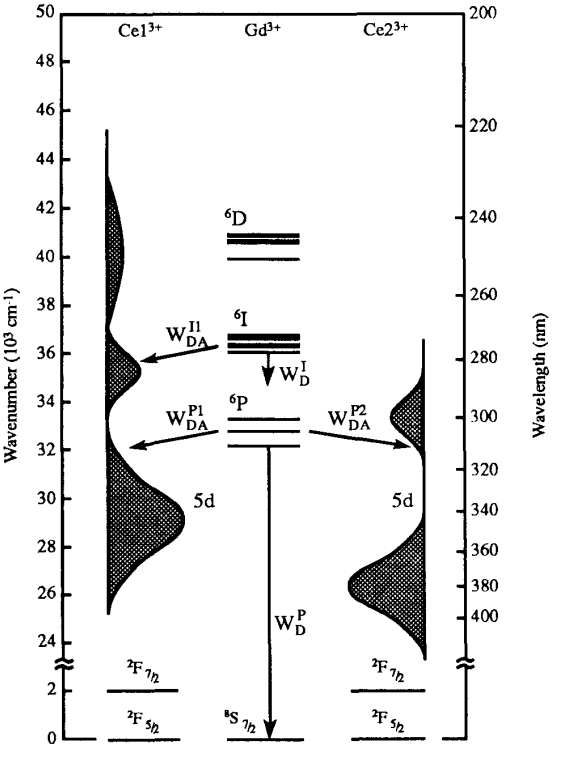

Fig. 1. Energy levels of Gd^{3+}, $Ce1^{3+}$ and $Ce2^{3+}$. W_{DA}^{I1} indicates the effective transfer rate from the ^6I_J multiplets of Gd^{3+} to $Ce1^{3+}$, W_{DA}^{P1} represents the rate from the ^6P_J multiplets of Gd^{3+} to $Ce1^{3+}$, and W_{DA}^{P2} indicates the rate from the ^6P_J multiplets of Gd^{3+} to $Ce2^{3+}$.

0-7803-1487-5/94$04.00©1994IEEE

We observed two types of excitation and emission spectra and two decay constants.

We also investigated the primary processes [2], [5]. The gamma-ray excited decay curve of GSO at room temperature has build-up and slow decay components. Since $Ce1^{3+}$, which is dominant at room temperature, has a single exponential decay (22~25 ns), the observed slow decay is attributed to slow energy transfer from the gamma rays to the Ce^{3+}, i.e., a slow primary process, which may be due to the resonant energy transfer from Gd^{3+} to Ce^{3+}, since the excited states of Gd^{3+} overlap the absorption bands of Ce^{3+} (fig. 1).

II. MODEL

We apply the theory of energy transfer developed by Burshtein et al. [8-10] to GSO, assuming that the energy transfer from Gd to Ce in GSO is dominantly non-radiative (resonant) and the back transfer from Ce to Gd can be neglected [5]. When donor-donor (Gd-Gd) energy transfer exists with donor-acceptor (Gd-Ce) transfer, the donor decay becomes complex. After short-pulse excitation of the donor system (Gd^{3+}), the decay processes of the excited donor decay can be divided into three stages [11]: (1) Static ordered decay; (2) Static disordered decay; (3) Migration-limited decay. In stage (1), the excited donors, which have nearby acceptors, decay rapidly, and the donor decay becomes exponential. In stage (2), the excited donors transfer their energy to acceptors located farther away, and the donor decay becomes non-exponential. In both of these stages, the D-A transfer probabilities are independent of donor density, N_D. In stage (3), the D-A energy transfer is preceded by energy migration among Gd^{3+} ions, where energy localized at a particular Gd^{3+} ion migrates through the Gd^{3+} sublattice until a Gd^{3+} ion transfers its energy to a Ce^{3+} ion. In this stage the Gd^{3+} decay again becomes exponential.

Since the Gd-Gd nearest neighbor distance is small (~3.57 Å), the Gd-Gd transfer rate must be very high [12]; thus, the decay of the excited donors rapidly becomes exponential. Here we assume that stage (3) dominates on our time scale. As the Gd concentration decreases by partial substitution of Y or Lu, the Gd-Gd separation increases, and the strength of the resonant energy transfer between Gd^{3+} ions is reduced. This dilution slows the migration of the excitation and lengthens the time for the energy to reach the Ce^{3+}. The net result is that the excited Gd^{3+} lifetime increases monotonically as the Gd^{3+} concentration decreases.

For a particular pair of ions we define the D-D transfer rate as W_{dd}, and the D-A transfer rate as W_{da}. The notation for the transfer rates are [8]: $W_{dd} = C_{dd}\ f(R)$ and $W_{da} = C_{da}\ f(R)$, where R is the distance between interacting ions and f(R) are functions whose forms are determined by the nature of the D-D and D-A interactions. C_{dd} and C_{da} are microscopic parameters for the D-D and D-A interactions, respectively. In stage (3), the macroscopic transfer rate from Gd^{3+} to Ce^{3+} can be described by an effective transfer rate (W_{eff}). If the donor and acceptor ion densities are defined as N_D and N_A, the effective transfer rate W_{eff} is a function of four parameters [8]: C_{dd}, C_{da}, N_D, and N_A. W_{eff} linearly depends on N_A regardless of the type of interaction (multipolar or exchange) between the donors or between the donor and the acceptor. If both interactions are dipole-dipole, W_{eff} also linearly depends on the donor density N_D, i.e., W_{eff} depends linearly on the product $N_A \times N_D$. The exact form of W_{eff}, however, varies depending on the type of migration [10].

We choose the excited ^6I_J multiplets of Gd^{3+} in analyzing the energy transfer mechanism from Gd to Ce. The different multiplets of ^6I_J states are treated together since we are not concerned with the detailed optical properties. The transfer rate from ^6P_J multiplets of Gd^{3+} to $Ce1^{3+}$ in GSO is low [2] and is difficult to analyze on the relatively short time scale (< 170 ns) of our UV excitation experiments. Transfer from the higher excited states of Gd^{3+} (e.g. ^6D_J and ^6G_J) was not considered in the present analysis.

When we analyze the energy transfer from the ^6I_J multiplets of Gd^{3+} to Ce^{3+}, we ignore the transfer from Gd^{3+} to $Ce2^{3+}$ since its spectral overlap is very small (fig. 1). The rate equations for Gd^{3+} and $Ce1^{3+}$ are given by [13]:

$$\frac{dN_D^{I*}}{dt} = -W_D^I N_D^{I*} - W_{DA}^{I1} N_D^{I*} \quad \text{and} \tag{1}$$

$$\frac{dN_A^*}{dt} = -W_A N_A^* + W_{DA}^{I1} N_D^{I*} \ , \tag{2}$$

where N_D^{I*} and N_A^* are the number of excited ^6I_J multiplets and excited acceptors ($Ce1^{3+}$), respectively. W_{DA}^{I1} is the effective transfer rate from the ^6I_J multiplets of Gd^{3+} to $Ce1^{3+}$, W_D^I is the decay rate of the lowest ^6I_J multiplets including transitions to both ground $^8S_{7/2}$ state and the excited ^6P_J multiplets in an isolated Gd^{3+} ion, and W_A is the decay rate of the excited 5d level of $Ce1^{3+}$. The solution for N_A^* is:

$$N_A^*(t) = N_D^{I*}(0)\frac{W_{DA}^{I1}}{W_A - (W_D^I + W_{DA}^{I1})}$$

$$\times \{\exp[-(W_D^I + W_{DA}^{I1})\,t] - \exp[-W_A\,t]\} \ , \tag{3}$$

where $N_D^{I*}(0)$ is the initial number of excited donors (^6I_J multiplets). Eq. (3) describes the $Ce1^{3+}$ decay when no $Ce1^{3+}$ ions are created at t=0. Here we measured the decay of $Ce1^{3+}$ emission (N_A^*) and determined the decay rate of the excited ^6I_J multiplets of Gd^{3+} ($W_D^I + W_{DA}^{I1}$) as a function of N_A and N_D using UV- and gamma-ray excitations.

III. EXPERIMENT

The crystals were grown by the Czochralski technique using raw materials (Gd_2O_3, Y_2O_3, Lu_2O_3, and CeO_2), which are at least 99.99% purity and with GSO seed crystals. The starting melt material had chemical compositions $(Gd_{1-x-y}Ce_xY_y)_2(SiO_4)O$ or $(Gd_{1-x-y}Ce_xLu_y)_2(SiO_4)O$. The crystal's

structure was analyzed by the X-ray diffraction. The chemical composition was analyzed by X-ray Assay Laboratory using inductively-coupled plasma mass spectrometry.

The crystal structure changes from $P2_1/c$ to C2/c by partially substituting the smaller rare earths, Y^{3+} (0.910 Å) and Lu^{3+} (0.848 Å), into Gd^{3+} (0.938 Å) sites. This change produces different crystal field and space group, as well as the different energy splitting of the 4f-5d transitions of Ce^{3+}. Here we, therefore, focused only on 10 diluted GSO samples, which have the monoclinic structure $P2_1/c$ with relatively low Y (or Lu) concentration ($y \leq 0.28$) (table I). The ratio of the Gd, Y, and Lu in the crystals were approximately (within 12%) the same as in the melt. The distribution coefficient of Ce varied from ~0.55 to ~0.81. The data obtained from undiluted GSO samples [5] were also used.

The optical equipment configuration and the refrigeration system has been described previously [4]. The UV excited decay curves of the diluted GSO crystals were measured using the U9B beam line of National Synchrotron Light Source at Brookhaven National Laboratory (pulse width ~1.0 ns). The details of the experimental set up are described elsewhere [5]. The gamma-ray excited decay curves were measured with a ^{137}Cs source. Both UV- and gamma-ray excited decay curves were obtained with the time-correlated single photon technique [14], and the data were analyzed with a least squares fitting routine. When diluted GSO crystals are excited by gamma rays, both Ce1 and Ce2 emit photons at room temperature. To measure selectively the decay curve of Ce1 (emission peak at 425 nm), a bandpass filter (CORION S40-400) was placed between the crystal and the stop photomultiplier. This filter (transparent at ~400 nm) eliminates Ce2 emission (emission peak at 480 nm).

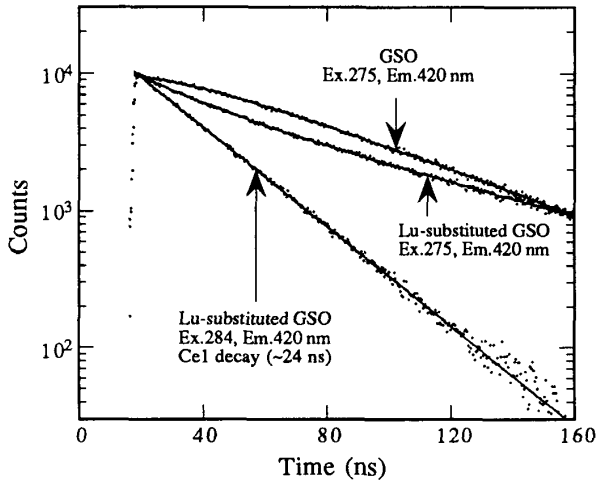

Fig. 2. UV-excited decay curves of $(Gd_{0.99}Ce_{0.0018})_2(SiO_4)O$ and $(Gd_{0.76}Ce_{0.0015}Lu_{0.24})_2(SiO_4)O$ (crystal no. 9). The data are fit with a single exponential (~24 ns) or eq. (4) (solid line).

Table I

Chemical compositions in diluted GSO, and decay rates of the excited Gd^{3+} states (^6I_J and ^6P_J) calculated from the decay curve fits (eqs. (4) and (5)). The fifth column is the decay rate ($W_D^I + W_{DA}^{II}$) of the excited ^6I_J multiplets obtained from the UV-excited decay curve. The sixth and seventh columns are the decay rates of the ^6I_J and ^6P_J multiplets calculated from gamma-ray excited decay curves. Decay rates are given by their reciprocals.

no.	Chemical composition $[Gd_{1-x-y}Ce_x(Y \text{ or } Lu)_y]_2SiO_5$			^6I_J (ns)	^6I_J (ns)	^6P_J (ns)
	1-x-y	x	y	(UV)	(γ)	(γ)
1	0.96	0.0015	0.044(Y)	51	57	440
2	0.94	0.0038	0.056(Y)	33	34	395
3	0.94	0.0061	0.055(Y)	21	23	300
4	0.78	0.0016	0.22(Y)	60	74	538
5	0.72	0.0032	0.28(Y)	45	53	527
6	0.72	0.0054	0.28(Y)	30	37	370
7	0.95	0.0014	0.049(Lu)	60	61	485
8	0.84	0.0017	0.16(Lu)	59	67	567
9	0.76	0.0015	0.24(Lu)	73	85	634
10	0.75	0.0034	0.25(Lu)	48	61	491

IV. RESULTS AND DISCUSSION

First, the emission and excitation spectra of 10 diluted GSO crystals were investigated using UV-excitation at room temperature. Although the emission and excitation bands of Ce2 were not well resolved because of thermal quenching, the bands of Ce1 were observed at almost the same wavelengths as observed for undiluted GSO (containing neither Y nor Lu). That is, the excitation bands of Ce1 were at 250, 284, and 345 nm (fig. 1). The emission band of Ce1 was at 425 nm [4].

The decay curves of the 10 diluted GSO samples were measured with excitation wavelengths of 275 nm (into ^6I_J multiplets) and 284 nm (directly into $Ce1^{3+}$ band), and an emission wavelength of 420 nm. All the decay curves excited at 284 nm could be fit with a single exponential (~24 ns) (fig. 2). That is, $W_A^{-1} = 24$ ns. Decay curves excited at 275 nm show different amounts of build-up. Fig. 2 shows two such decay curves from samples with approximately the same Ce concentration but different Gd concentrations. As expected, Lu-substituted GSO has a slower build-up, which suggests slower migration through the Gd^{3+} sublattice. Since at 275 nm both Gd^{3+} and $Ce1^{3+}$ are excited, the decay curves excited at 275 nm were fit with the following equation:

$$N_A^*(t) = N_A^*(0)\exp\left(-\frac{t}{24}\right) + N_D^{I*}(0)\frac{W_{DA}^{II}}{\frac{1}{24} - (W_D^I + W_{DA}^{II})} \times \{\exp[-(W_D^I + W_{DA}^{II})t] - \exp[-\frac{t}{24}]\}, \quad (4)$$

where the first term represents direct Ce1 emission, and the second term represents delayed Ce emission after energy transfer from Gd. $N_A^*(0)$ is the number of excited acceptors at t=0.

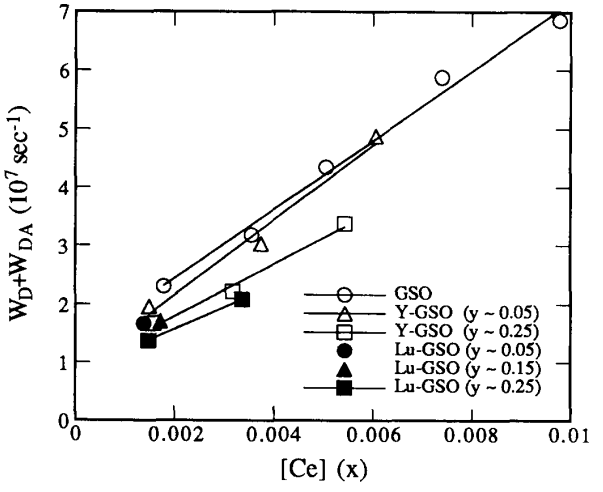

Fig. 4. The decay rates of the ^6I_J multiplets obtained from UV-excited decay curves. The measured samples are undiluted GSO (y = 0 and x varies from 0.0018 to 0.0098) and diluted GSO (crystal no. 1 ~ 10).

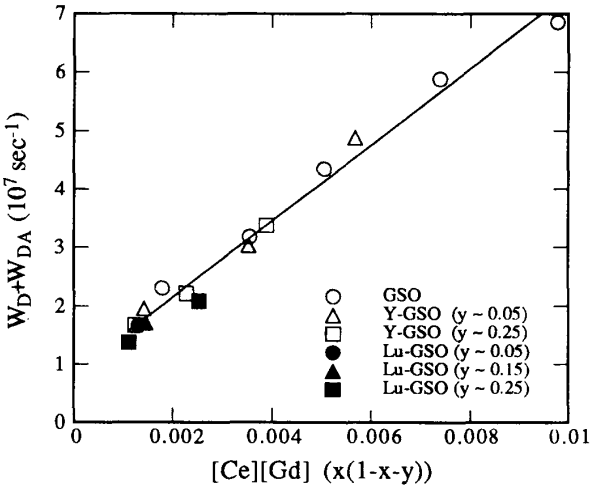

Fig. 5. The same decay rates as in fig. 4, but displayed as a function of [Ce]×[Gd].

The decay rates ($W_D^I + W_{DA}^{I1}$) of the ^6I_J multiplets of Gd^{3+} for 10 samples are shown with previous data for undiluted GSO (y = 0) as a function of Ce concentration (fig. 4). Ce^{3+} was not measured, so we assume that the $Ce1^{3+}$ concentration is proportional to the total Ce concentration. The decay rates ($W_D^I + W_{DA}^{I1}$) are fit with a straight line for a group of samples which have approximately the same Gd concentration. The decay rates of the diluted GSO samples which have the same Gd concentration linearly increase with the Ce concentration, in agreement with the functional dependence of the effective transfer rates W_{DA}^{I1}. The straight lines intercept the vertical axis at about 1×10^7 sec^{-1}. This indicates that W_D^I is about 1×10^7 sec^{-1}. Since the lowest state of the ^6I_J multiplets, i.e., $^6I_{7/2}$ usually has a decay rate of the order of $10^3 \sim 10^4$ sec^{-1} [15], this large value of W_D^I may represent the energy transfer rate from Gd to impurity centers or to quenching centers, whose contribution is not included in eq. (4). The existence of quenching centers such as Gd^{3+} traps (or perturbed Gd^{3+} ions) in Gd compounds has been reported [16], [17]. In fact, when a lightly Ce-doped GSO crystal was cooled to 11 K, we observed very strong emission at 318 nm. This wavelength is slightly longer than the peak wavelength of unperturbed Gd^{3+} ions (excited $^6P_{7/2}$ level) and can be attributed to perturbed Gd^{3+} ions or Gd^{3+} traps. This emission disappeared at temperatures above 60 K.

For the same Ce concentration, the decay rates ($W_D^I + W_{DA}^{I1}$) decrease as the Gd concentration decreases (fig. 4). This dependence of the decay rates on the Gd concentration suggests that the donor decay is in stage (3), since the transfer rates from Gd to Ce in stages (1) and (2) are independent of the Gd concentration. This dependence also suggests that the dilution of Gd causes a longer migration time through the Gd and results in slower energy transfer to Ce.

Although we do not know the nature of the Gd-Gd and the Gd-Ce interactions in GSO, we attempted to correlate the decay rates with Gd concentration by plotting the decay rates vs. the product of Ce concentration and Gd concentration, [Ce]×[Gd] (fig. 5). The decay rates have a linear relationship, suggesting that both Gd-Gd and Gd-Ce interactions for the excited ^6I_J multiplets are dipole-dipole in nature.

The gamma-ray excited decay curves were also measured for the 10 diluted GSO samples. The Ce2 emission, which is weak but has a fast decay constant (~5 ns) [2], is eliminated with the bandpass filter. As Gd concentration decreases with the partial substitution of Lu, the decay of $Ce1^{3+}$ becomes slower, which again agrees with our assumption. We fit the gamma-ray excited decay curves [5] with the following equation:

$$N_A^*(t) = N_A^*(0)\exp(-\frac{t}{24}) + N_D^{I*}(0)\frac{W_{DA}^{I1}}{\frac{1}{24} - (W_D^I + W_{DA}^{I1})} \times \{\exp[-(W_D^I + W_{DA}^{I1})t] - \exp[-\frac{t}{24}]\}$$

$$+ N_D^{P*}(0)\frac{W_{DA}^{P1}}{\frac{1}{24} - (W_D^P + W_{DA}^{P1} + W_{DA}^{P2})} \times \{\exp[-(W_D^P + W_{DA}^{P1} + W_{DA}^{P2})t] - \exp[-\frac{t}{24}]\} \quad (5)$$

which is based on the assumption that after gamma rays are absorbed in the crystal, excited Ce^{3+} ions, $(Ce^{3+})^*$, and excited Gd^{3+} ions, $(Gd^{3+})^*$, are immediately created. We assume that the build-up of the gamma-ray excited decay is due to the energy transfer from ^6I_J multiplets of Gd^{3+} to $Ce1^{3+}$, and that the slow decay is due to the transfer from ^6P_J multiplets of Gd^{3+} to $Ce1^{3+}$ and $Ce2^{3+}$, whose decay equation is not shown. We thus ignore the energy transfer from other excited states of

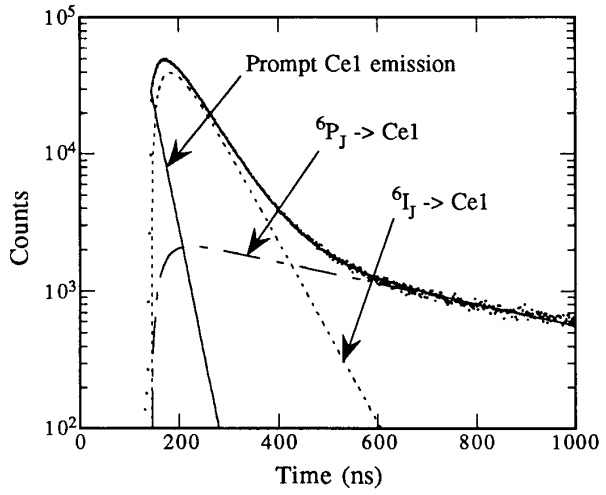

Fig. 6. The gamma-ray excited decay curve of crystal (no. 8). The data are fit with eq. (5) and decomposed into three curves.

Gd^{3+} to Ce^{3+} in this model of the scintillation processes. The first term in eq. (5) indicates the prompt Ce1 emission, the second term represents Ce1 emission through the ^6I_J multiplets of Gd^{3+}, and the third term represents Ce1 emission through the ^6P_J multiplets. $N_A^*(0)$, $N_D^{I*}(0)$, and $N_D^{P*}(0)$ are the populations of excited Ce1 and of the excited ^6I_J and ^6P_J multiplets, at t=0. The last two terms are the delayed Ce1 emission. The fitting curve for the decay of crystal (no. 8) is shown (fig. 6). The decay rates of the ^6I_J multiplets $(W_D^I + W_{DA}^{I1})$ and those of the ^6P_J multiplets $(W_D^P + W_{DA}^{P1} + W_{DA}^{P2})$ calculated from the gamma-ray excited decay curves are shown (table I). The decay rates of the ^6I_J multiplets agree well with the decay rates obtained with UV excitation for lightly diluted GSO ($y \leq 0.16$) (table I). However, the differences in the decay rates between UV- and gamma-ray excitation increase for more heavily diluted crystals ($y \sim 0.25$). The reasons for this difference are not clear.

The decay rates of the ^6I_J multiplets obtained from the gamma-ray excited decay curves of the heavily diluted GSO are much longer than the decay rates from UV-excited decay curves. Since for undiluted GSO the decay rates between UV- and gamma-ray excitation agree [5], the longer decay rates obtained with gamma-ray excitation for diluted GSO must be related to the substitution of Y and Lu. Lempicki et al. [18] reported the presence of the slow energy transfer to the Ce^{3+} in the gamma-ray excited decay curve of YPO_4:Ce. Although they didn't observe slow decay components for $LuPO_4$:Ce, the substitution of Y and Lu into GSO may introduce other channels which slowly transfer energy to either Gd^{3+} or Ce^{3+} when diluted GSO is exposed to ionizing radiation.

V. SUMMARY

The decay rate of the ^6I_J multiplets of Gd^{3+} was investigated for Y- or Lu- substituted GSO using UV- and gamma-ray excitations. The decay rates obtained with two different excitation methods for lightly diluted GSO samples agree and suggest that the migration through the Gd slows down with the substitution of Y or Lu and leads to a delay in the overall transfer rate from Gd to Ce. The decay rates obtained from UV excitation have a linear dependence on the product [Ce]×[Gd], which suggests that both Gd-Gd and Gd-Ce interactions for the excited ^6I_J multiplets have dipole-dipole character. The decay rates obtained with UV excitation have a term independent of the Ce concentration, which suggests the existence of impurity centers or quenching centers. We, in fact, observe strong emission which is different than regular Gd^{3+} emission and attribute it to a Gd trap. A large difference in the decay rates between UV- and gamma-ray excitation was observed for heavily diluted GSO, which suggests that the substitution of Y and Lu introduces other channels of energy transfer when the diluted GSO is excited by gamma-ray radiation.

REFERENCES

[1] K. Takagi and T. Fukazawa, Appl. Phys. lett., vol. 42, no. 1, pp. 43-45, 1983.
[2] H. Suzuki, T. A. Tombrello, C. L. Melcher and J. S. Schweitzer, J. Lumin. in press.
[3] C. L. Melcher, J. S. Schweitzer, T. Utsu and S. Akiyama, IEEE Trans. Nuc. Sci. NS-37, no. 2, pp.161-164, 1990.
[4] H. Suzuki, T. A. Tombrello, C. L. Melcher and J. S. Schweitzer, Nucl. Instr. and Meth., vol. A320, pp. 263-272, 1992.
[5] H. Suzuki, T. A. Tombrello, C. A. Peterson, C. L. Melcher and J. S. Schweitzer, "The role of Gd in the scintillation processes of $Gd_2(SiO_4)O$:Ce," to be submitted.
[6] J. B. Birks, The theory and practice of scintillation counting, Pergamon Press, 1964, pp. 55-56.
[7] J. Felsche, The crystal chemistry of the rare-earth silicates, in: Structure and Bonding V13, Springer-Verlag, 1973, pp. 99-197.
[8] I. A. Bondar et al., Sov. Phys. JETP, vol. 54, no. 1, pp.45-54, 1981.
[9] A. I. Burshtein, J. Lumin., vol. 34, pp. 167-188, 1985.
[10] A. I. Burshtein, Sov. Phys. Usp., vol. 27, no. 8, pp. 579-606, 1984.
[11] A. J. de Vries, B. P. Minks and G. Blasse, J. Lumin., vol. 39, pp. 153-160, 1988.
[12] H. S. Kiliaan, A. Meijerink and G. Blasse, J. Lumin., vol. 35, pp. 155-161, 1986.
[13] B. Henderson and G. F. Imbusch, Optical Spectroscopy of Inorganic Solids, Clarendon Press, 1989, chap. 10.
[14] L. M. Bollinger and G. E. Thomas, Rev. Sci. Instr., vol. 32, no. 9, pp. 1044-1050, 1961.
[15] J. Sytsma, G. F. Imbusch and G. Blasse, J. Phys.: Condens. Matter, vol. 2, pp. 5171-5178, 1990.
[16] A. J. de Vries and G. Blasse, J. Phys. (Paris) C7, pp. 109-112, 1985.
[17] C. T. Garapon, B. Jacquier, J. P. Chaminade and C. Fouassier, J. Lumin., vol. 34, pp. 211-222, 1985.
[18] A. Lempicki, E. Berman, A. J. Wojtowicz, M. Balcerzyk and L. A. Boatner, IEEE Trans. Nuc. Sci., vol. 40, pp. 384-387, 1993.